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Inventor(s):

EDWARDS KEITH ANDREW; LENG CHRISTINE ANN; SAMS PHILIP JOHN ;

Applicant(s): UNILEVER PLC (GB); UNILEVER NV (NL) ;

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ABSTRACT:

A wiping article consists of two porous substrate layers sandwiching surfactant. The surfactant is chosen so that its properties retard its release when the article is wet and squeezed, hence avoiding initial excess foaming and lengthening the number of times that a foaming solution of surfactant can be squeezed from the article. The surfactant is chosen to have a Krafft temperature above 20 DEG C and/or form a liquid crystalline phase at temperatures above its Krafft temperature up to 30 DEG C preferably up to 50 DEG C.

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71 Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ (GB)

84 Designated Contracting States: **GB**

71 Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam (NL)

84 Designated Contracting States:
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72 Inventor: **Edwards, Keith Andrew**
46 Rosefield Avenue Bebington
Wirral Merseyside L63 5JT (GB)

Leng, Christine Ann
25 Longmeadow Gatton
Wirral Merseyside (GB)

Sams, Philip John
Cranford Briardale Road
Willaston South Wirral LL4 1TB (GB)

74 Representative: **Ford, Michael Frederick et al**
MEWBURN ELLIS 2 Cursitor Street
London EC4A 1BQ (GB)

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Description

WIPING ARTICLE

The invention relates to a wiping article suitable for use in cleaning soiled surfaces in the presence of water. The wiping article can be adapted for cleaning hard surfaces, particularly those to be found in the domestic kitchen and bathroom, or for cleaning the surface of the human body, for instance when taking a shower.

There have been a number of prior proposals for impregnated wiping articles for hard surfaces e.g. DE 2325176 (Schickedanz), EP 66463 (Unilever) and EP 211664 (Unilever). There have also been prior proposals for impregnated "cloths" for washing the human body surface, e.g. EP 68516 (Barbey & Hecken) and US 4303543 (Procter & Gamble). EP 161911 (Unilever) is relevant to both applications.

It has been proposed, e.g. in the above-mentioned EP 66463 and EP 211664, to provide a hard surface wiping article as a sandwich structure with first and second substrate layers sandwiching a core of concentrated surfactant.

A problem which can arise with both the above-mentioned categories of wiping article is that when used in the presence of a substantial quantity of water the soap or detergent active with which they are impregnated is leached out too quickly, leaving the article prematurely exhausted of soap or detergent active. This might for instance be manifested as a hard surface wipe being exhausted after a single use, or a wipe intended for use under the shower failing to complete a single use.

EP 161911 proposed to delay release of impregnating detergent active compound by means of moisture barrier areas, applied in a pattern to sandwich the detergent active applied in a similar pattern and retarding the leaching of the detergent active from the wipe.

Our EP 211664, mentioned above, proposed a wiping article for hard surfaces in which surfactant was trapped in a polymeric matrix material, thereby conferring controlled release properties.

We have now found that release of surfactant can be retarded in a simpler way.

According to the present invention there is provided a substantially dry-to-the-touch wiping article which is suitable for use in cleaning soiled surfaces in the presence of water, the article comprising first and second substrate layers with surfactant in solid form sandwiched between them, characterised in that the surfactant

- i) forms a liquid crystalline phase in contact with water at temperatures above its Krafft temperature and up to at least 30°C, and/or
- ii) has a Krafft temperature above 20°C.

Use of a surfactant with a Krafft temperature above 20°C (which is a relatively high Krafft temperature) has the consequence that the surfactant will have poor solubility, and be slow to dissolve, when contacted by water at temperatures up to about the Krafft temperature. This can provide slow release of surfactant when the wiping article is used with cold or lukewarm water.

Preferable, however is formation of a liquid crystal phase when the surfactant comes into contact with water, especially formation of a cubic or hexagonal, most preferably hexagonal, liquid crystal phase. Such liquid crystal phase(s) will form at appropriate points in the concentration gradient between surfactant in the wiping article, and water permeating into the article. Formation of a hexagonal liquid crystal phase when water contacts the solid surfactant is particularly effective in delaying release of surfactant from the wiping article because the liquid crystal phase is highly viscous and is itself slow to dissolve in water, moreover it forms a temporary shield between the remaining solid surfactant and any water.

Formation of a liquid crystal phase will serve to retard dissolution when the wiping article is contacted by water at any temperature at which the liquid crystal phase exists. Desirably this is from 20°C or the surfactant's Krafft temperature (whichever is greater) upwards to at least 30°C preferably 35 or 40°C and still better up to 50°C which is approximately the highest temperature which hands can bear. Thus, for forms of the invention in which a liquid crystal phase serves to retard dissolution, either the surfactant will display a Krafft temperature below 20°C with liquid crystal phase existing over a range of temperatures extending at least from 20°C to 30°C, or the surfactant will display a Krafft temperature above 20°C with liquid crystal phase existing over a range of temperatures extending upwards from the Krafft temperature and reaching a temperature which is at least 30°C.

It is important that the surfactant should foam in water, because this provides the user with visual confirmation of the presence of surfactant. For a surfactant with a fairly high Krafft temperature, a fairly high critical micelle concentration would be desirable in order that the surfactant should foam. It is preferred that the critical micelle concentration should be at least 2mMole/litre, better at least 4 or 5mMole/litre.

The surfactant needs to be in the form of a solid, so that it remains in place within the wiping article, when the article is dry.

It is strongly preferred that the surfactant itself can exist as a solid at 20°C, preferably at temperature up to at least 25°C. This makes it possible to incorporate solid concentrated surfactant between the two layers of substrate, and have the surfactant stay in place during storage of the dry wiping article before use. Preferably the solid surfactant should not be sticky, more preferable is that the surfactant is able to exist as dry particles at 20°C, preferably at temperatures of at least 25°C. The surfactant may well be used in particulate form, with the particles trapped between the two substrate layers.

If the surfactant is used in particulate form, then the rate of dissolution may be adjusted to some extent by choice of the size of the surfactant particles.

The surfactant may be a non-soap detergent. Several types can be used. One possible type of surfactant is C₁₄ to C₁₆ sulphobetaines. These readily form hexagonal liquid crystal phases on contact with water. When dry they are crystalline solids.

Preferred surfactants for this invention are mild to the skin, e.g. monoalkyl sulphosuccinates or fatty acyl isethionates where the alkyl or acyl group has from 8 to 22 carbon atoms, preferably 10 to 16 carbon atoms. This anionic surfactant must have a solubilising cation, and alkali metal ions are preferred. In their commercially available forms, these types of surfactant frequently contain fatty acids and other impurities, but this does not reduce their usefulness in the present application.

Particularly preferred is sodium cocoyl isethionate which has a Krafft temperature of 26°C. Above the Krafft temperature both hexagonal and lamella liquid crystal phases form in the concentration gradient between the surfactant and water. When this surfactant is used, at temperatures below the Krafft temperature, there is restricted solubility in water and hence slow rate of dissolution. Above the Krafft temperature the hexagonal liquid crystal phases retards solution. The hexagonal liquid crystal phase exists from the Krafft temperature up to well over 50°C.

As indicated above the invention requires substrate layers. It is substrate layers which provide the wiping surfaces, and which give the article its strength and integrity.

The material of at least one substrate layer must be water permeable. Preferably the substrate layers are sheets of fibrous material.

Particularly preferred is a non-woven fibrous sheet. Cellulose fibres are particularly suitable in view of their ability rapidly to absorb water when employed to clean a soiled surface.

The substrate layers can also comprise other fibrous materials such as polyamide, polyester and polypropylene, or mixtures of such fibres, which are particularly useful in providing the article with extra wet strength.

The wet strength of substrate layer material can also be increased by incorporation of suitable binders such as styrene butadiene lattices, or an acrylic binder, or polyvinyl acetate, or polymer emulsions.

The absorbent substrate can be made from paper, in which case it will generally comprise cellulose fibres which are relatively short in length. Additives, such as hydroxyethyl cellulose may be employed to provide added wet strength.

The substrate layers may be the same or may be different. It can be advantageous to employ different substrate layers, for example choosing one substrate material to provide good wet strength and another substrate material to provide good absorbency. One preferred substrate material is a non-woven comprising cellulose fibres an example of which is Mitsubishi TCF 408, a 100% cuprammonium rayon spun bonded non-woven having the following technical specifications:

Nominal basis weight (g/m ²)	82.5
Thickness (μm)	500
Dry tensile strength: machine direction (N/m)	635
Dry tensile strength: cross direction (N/m)	565
Wet tensile strength: machine direction	498
Wet tensile strength: cross direction (N/m)	447
Absorption capacity (g/g)	5

Another substrate material is a non-woven comprising cellulose fibres such as Storalene 715:50 or Storalene 717:50 available from Stora-Kopparberg, Sweden, which contains the following ingredients:

% per w/w	
Cellulose fibres (wood pulp)	33
Cotton linters	29
Rayon	17
Polyamide	4
Binder*	17

*Storalene 715:50 contains an acrylic binder and Storalene 717:50 contains a polyvinyl acetate binder.

The relevant technical specification of Storalene 715:50 and Storalene 717:50 are set out below:

		Storalene	
		715:50	717:50
5	Nominal basis weight (g/m ²)	50	50
	Thickness (µm)	400	365
10	Dry tensile strength-machine direction (N/m)	600	625
	Dry tensile strength-cross direction (N/m)	450	330
15	Wet tensile strength-machine direction (N/m)	300	205
20	Wet tensile strength-cross direction (N/m)	250	95
25	Absorption capacity (g/g)	4	4

30 A further example of a suitable substrate material is Hi-Loft 3051 available from Scott Paper Co, a random wet-laid lofty paper web having a base weight of 82 g/m² and a porosity of 92%. This is bulky high-porosity sheet material having a high wicking rate.

It is possible for a substrate layer to consist of a laminate of more than one layer, for example a laminate of an absorbent material with a reinforcing material at the exterior surface. It is possible for abrasive particles to be applied to the exterior surface of one or both substrate layers. Suitable abrasive particles are polyvinyl chloride granules. The application of abrasive granules to the exterior surface of a wiping article is described in our published European application EP 211664.

40 Abrasive material may be applied to the exteriors of both substrate layers, and possibly different abrasive materials could be employed so that one substrate layer provided a harsher abrasive surface than the other. Preferable however is to have abrasive on one substrate layer and a smooth surface on the other substrate layer making it suitable for polishing off after initial cleaning with the abrasive side of the wiping article.

Joining two substrate layers with surfactant sandwiched between them may be accomplished in various ways. It may be carried out by heat sealing the two layers to each other with a regular pattern or array of heat sealing, as described for instance in EP 66463 and EP 112654. Alternatively the substrate layers may be joined by use of sintered polyethylene in the manner described in our copending application [case C3263] filed simultaneously with this application and claiming priority from British application 8817727.4.

Examples

50 In these Examples, wiping articles were prepared by a standard procedure, in which particles of surfactant were sandwiched between substrate layers. One substrate layer consisted of Mitsubishi TCF 408 mentioned above and the other consisted of Hi-Loft 3051 also mentioned above. To manufacture the wiping article, squares of each substrate material, 30cm along each side were employed. 2.5g polyethylene beads of maximum size 0.3mm were sprinkled over one surface of each square of substrate and the substrate then heated in an oven to melt the beads sufficiently to bond to the substrate layer. A portion of powdered surfactant was then sprinkled over a 27.5cm x 27.5cm portion of the polyethylene-coated surface of one substrate layer, the other substrate layer was then superimposed so that the polyethylene-coated surfaces were confronting each other and sandwiching the surfactant. Then the assembly was passed between heated rollers to effect heat-sealing between the polyethylene layers. The resulting laminate was then trimmed to a square of 28cm along each side.

60 In this fashion wiping articles were prepared using several surfactant materials and several dosages of each surfactant material. The surfactants employed in these Examples were:
sodium dodecyl sulphate whose Krafft temperature and critical micelle concentration are reported as 16°C and 8mMoles/litre in Surfactants and Interfacial Phenomena, Milton Rosen, Wiley 1978 (other literature reports lower Krafft temperatures);

65 sodium dodecyl sulphonate for which the same reference quotes a Krafft temperature of 38°C and a critical

micelle concentration of approximately 10mMole/litre;
 sodium di C6-C8 alkylsulphosuccinate having a Krafft temperature of 15-18° C;
 sodium cocoyl isethionate (Effan AT 84G from Akzo Chemie) whose manufacturers state that it has a Krafft temperature of 26°C. Parris et al JAOCS 49 649 report a critical micelle concentration of approximately 6mMole/litre for the dodecyl component which predominates. This surfactant forms hexagonal liquid crystal phases (as well as lamella phases) on contact with water above the Krafft temperature. This isethionate was used in several different particle sizes which were obtained by grinding and sieving the commercial noodles of this surfactant.

Example 1

Wiping articles prepared as above, using various surfactants, were tested by a procedure to determine the number of times they could be wet and squeezed out before becoming exhausted of surfactant. This test was carried out as follows. 25g of water (tap water of approximately 10° French hardness at a temperature of 35-40° C) was poured on to a wiping article which was then squeezed, thereby squeezing out approximately half the water from the article. The water squeezed out was poured into a 100ml measuring cylinder and shaken for 5 seconds. Any surfactant dissolved from the wiping article would cause foaming. A foam volume greater than the volume of liquid in the measuring cylinder after standing for two minutes was regarded as adequate foaming. The procedure was repeated until the observed foaming ceased to be adequate. The number of cycles of wetting and squeezing out in this fashion before foaming ceased to be adequate are given in the table below, which also states the surfactant employed and its particle size.

TABLE

Surfactant	Cycles to Exhaustion		
	0.2g surfactant per article	0.5g surfactant per article	1.0g surfactant per article
C ₈ /C ₁₈ dialkylsulpho- succinate average 0.4mm	7	7.5	8
Dodecyl sulphate average 0.4mm	5	7	8
Cocoyl isethionate			
i) 0.18-0.35mm	4	6	7.5
ii) 0.35-0.5 mm	4	6	7.5
iii) 0.5-1.0 mm	5	8.5	11
iv) 1.0-1.7 mm	*	10	16

* inadequate foam

As can be seen from the table, with both sodium dodecyl sulphate and dialkylsulphosuccinate, which do not meet the requirements of this invention, the number of cycles before exhaustion was not greatly increased by increasing the amount of surfactant in the wiping article whereas with sodium cocoyl isethionate the number of cycles before exhaustion increased with increasing amounts of surfactant in the wiping article, indicating that the rate of dissolution of the surfactant was slower.

The particle size of the isethionate also had an effect: larger particles dissolving more slowly. With the largest particles of isethionate the rate of dissolution was so slow that 0.2g surfactant did not give adequate foaming at all. Even the higher loadings of the larger sizes gave poor foam on the first cycle of wetting and squeezing out.

For a preferred wiping article isethionate was used, applying 0.1g of particles smaller than 0.35mm and 0.4-0.9g of particles in the 0.5 to 1.0mm size range.

When the surfactant was sodium dodecyl sulphate the wiping articles appeared to be producing more foam than desired, and felt slimy, except when the amount of surfactant included in the wiping article was at the low (0.2g) level. This was also observed with the wiping articles having dialkylsulphosuccinate as surfactant. When sodium cocoyl isethionate was used as surfactant this over foaming and apparent slimy feel were less apparent than with the other two surfactants.

Example 2

A comparison was made between wiping articles made by the above general procedure, using sodium dodecyl sulphate in one case and sodium dodecyl sulphonate in the other. Both surfactants were sieved before the articles were made, so that the surfactant particles had a size no greater than 0.5mm.

The release of surfactant from the articles was tested by the following procedure. 25g of water (approximately 10° French hardness) at a temperature of 25°C was poured on to a wiping article. The article was squeezed, thereby squeezing out approximately half the water from the article. This water was collected. The cycle of wetting the article, squeezing and collecting the expressed water was carried out repeatedly. The concentration of surfactant in samples of the expressed water was determined by titration with hyamine, which is a cationic surfactant. The extent of foaming was also noted. Results are set out in the following Table.

No. of wetting and squeezing cycles	Dodecyl Sulphate		Dodecyl Sulphonate	
	Conc. of surfactant mMole/litre	Comments	Conc. of surfactant mMole/litre	Comments
1	52	Too much foam Slimy feel	10	Adequate foaming
2	31		5	
5	4.5	Adequate foam	8	
7			7	
10	1.3	Borderline foam	4	
11	0.8	Inadequate foam	7	
14			2.2	Border-line
15			1.7	Inadequate foam

The results with sodium dodecyl sulphonate showed some experimental variation, notably in the concentrations in the water expressed on the second and eleventh cycles.

However, the results clearly show that sodium dodecyl sulphate, whose Krafft temperature is below the temperature of the water used in the test and which does not exist as a liquid crystal phase at the test temperature, gave excessive initial release of surfactant. By contrast, sodium dodecyl sulphonate has its Krafft point above the test temperature and the release of surfactant was retarded, avoiding initial overfoaming and giving adequate foaming for a greater number of cycles of wetting and squeezing.

Example 3

Wiping articles were made by the above general procedure. The surfactant employed was sodium cocoyl isethionate having a particle size in the range from 0.5 to 1mm.

The release of surfactant was determined by the procedure of Example 2. This test was carried out twice, once using water at 25°C and once using water at 35°C. The results are set out in the following table.

No. of wetting and squeezing cycles	Conc. of surfactant mMole/litre	Comments	Conc. of surfactant mMole/litre	Comments	
	Temp. 25°C		Temp. 35°C		5
1	6	Adequate foam	14	Adequate foam	10
2			14		
5			7		
6	6				15
9	4				
11			2	Borderline	20
12			1	Inadequate foam	
13	4				25
17	2	Borderline foam			
18	1	Inadequate foam			30

With water at 25°C, just below the Krafft temperature, there was steady release of surfactant similar to the result with sodium dodecyl sulphate in Example 2. 35

With water at 35°C, which is above the Krafft temperature, the release of surfactant from the wiping article is slightly faster than at 25°C. Nevertheless it is a steady release, manifestly different from the rapid release of dodecyl sulphate in Example 2, because the surfactant forms a liquid crystal phase at the test temperature. 40

Example 4

Wiping articles were prepared using sodium cocoyl isethionate of various particle sizes as used in Example 1. 45

The release of surfactant on initial wetting was tested by the procedure used in Example 2. The test was carried out using water at 35°C. The concentration of surfactant in the water expressed after first wetting was determined and the results are as follows: 50

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	Surfactant loading per article	Conc. of Surfactant mMole/litre	Comments
5	0.5g of 0.5-1.0mm	3	Borderline foam
10	0.4g of 0.5-1.0mm +0.1g of 0.18-0.35mm }	13	Good foam
15	0.5g of 1.0-1.7mm	2	Borderline foam
	0.4g of 1.0-1.7mm 0.1g of 0.18-0.3mm }	7	Good foam
20	1.0g of 1.0-1.7	3	Borderline foam
25	0.9g of 1.0-1.7 0.1g of 0.18-0.35 }	14	Good foam

Thus use of a large particle size with a small amount of small particle size enables good foam on the first cycle of wetting and squeezing as well as achieving retarded release.

Claims

1. A substantially dry-to-the-touch wiping article which is suitable for use in cleaning soiled surfaces in the presence of water, the article comprising first and second substrate layers with surfactant in solid form sandwiched between them, characterised in that the surfactant
 - i) forms a liquid crystalline phase in contact with water at temperatures above its Krafft temperature and up to at least 30°C, and/or
 - ii) has a Krafft temperature above 20°C.
2. An article according to claim 1 wherein the pure surfactant is capable of existing in dry particulate form at 20°C.
3. An article according to any one of the preceding claims wherein the surfactant forms a hexagonal or cubic liquid crystalline phase on contact with water at temperatures above its Krafft temperature and up to at least 35°C.
4. An article according to claim 3 wherein the surfactant forms the liquid crystalline phase at temperatures up to at least 50°C
5. An article according to any one of the preceding claims wherein the surfactant is a salt of an acyl isethionate wherein the acyl group contains from 8 to 22 carbon atoms, the salt being formed by a solubilising cation.
6. An article according to claim 5 wherein the fatty acyl group is coconut acyl.
7. An article according to any one of the preceding claims wherein the surfactant has a critical micelle concentration of at least 2mMole/litre.
8. An article according to claim 7 wherein the critical micelle concentration is at least 4mMole/litre.